Electronic Supplementary Material (ESI) for CrystEngComm.

Cocrystal formation by Ionic liquid assisted grinding

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Supporting Information

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S1. Experimental Details

A. Materials

Caffeine, citric acid and glutaric acid were purchased from Sigma-Aldrich and used without further purification. All ionic liquids were obtained from Iolitec. All the ionic liquids were stored under vacuum in a glovebox and were filtered through a 0.2 μm PTFE membrane (with polypropylene housing) before using in grinding experiments.

B. Ionic Liquid Assisted Grinding Experiments (IL-AG)

(i) Caffeine-Citric Acid (CAF-CA)

At first, caffeine and citric acid were taken in 1: 1 molar ratio (CAF = 97.0±0.05 mg, CA = 96.13±0.05 mg) and placed in a mortar. Approximately, 40 μL of ionic liquids were used in each grinding experiment. The grinding time varied from 15-20 minutes. Each grinding experiment was repeated at least twice to confirm the structural outcome.

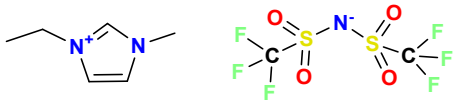
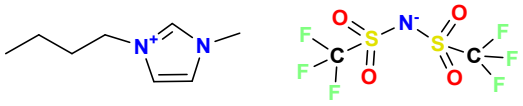
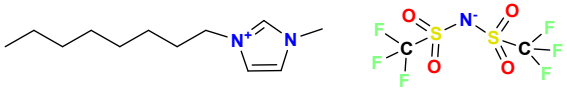
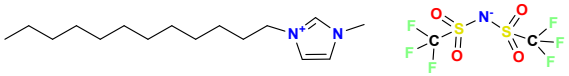
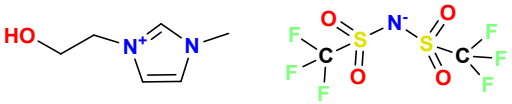
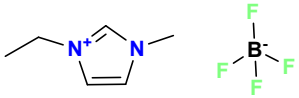
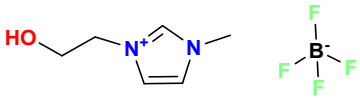
(ii) Caffeine-Glutaric Acid (CAF-GLU)

At first, caffeine and glutaric acid were taken in 1: 1 molar ratio and placed in a mortar (CAF = 97.13±0.08 mg, GLU = 66.08±0.08 mg). A volume of 40 μL of ionic liquids were used in each grinding experiment. The grinding time for each case was fixed around 15±1 minutes to enable comparative analysis. Each grinding experiment was repeated at least twice to confirm the structural outcome.

C. Powder X-Ray Diffraction (PXRD)

PXRD experiments were performed on all samples using a PANalytical X'Pert PRO diffractometer at 45 kV with an anode current of 40 mA. The instrument has a PW3050/60 standard resolution goniometer and a PW3373/10 Cu LFF DK241245 X-Ray tube. The $K_{\alpha 1}$ radiation of λ=1.540598 Å was used for all the experiments. In a typical experiment, samples were placed on a spinner stage in reflection mode and data were collected after spinning being enabled with a revolution time of 1.0 second. Settings on the incident beam path included soller slit of 0.04 rad, a fixed mask of 10 mm, a programmable divergence slit and a 1° anti-scatter slit. Settings on the diffracted beam path include a soller slit of 0.04 rad and a fixed 1/4° anti-scatter slit. A typical scan was set as a continuous scan with a scan range of 2θ = 3° to 2θ = 35°. The step size was 0.0020889°, and time per step was 5.080 seconds.

S2. Chemical Diagrams of imidazolium based ionic liquids

 [C_2mim][NTf_2]	 [C_4mim][NTf_2]
 [C_8mim][NTf_2]	 [C_{12}mim][NTf_2]
 [OHC_2mim][NTf_2]	 [C_2mim][BF_4]
 [OHC_2mim][BF_4]	

S3. Packing Diagrams of CAF-CA and CAF-GLU polymorphs discussed in the paper

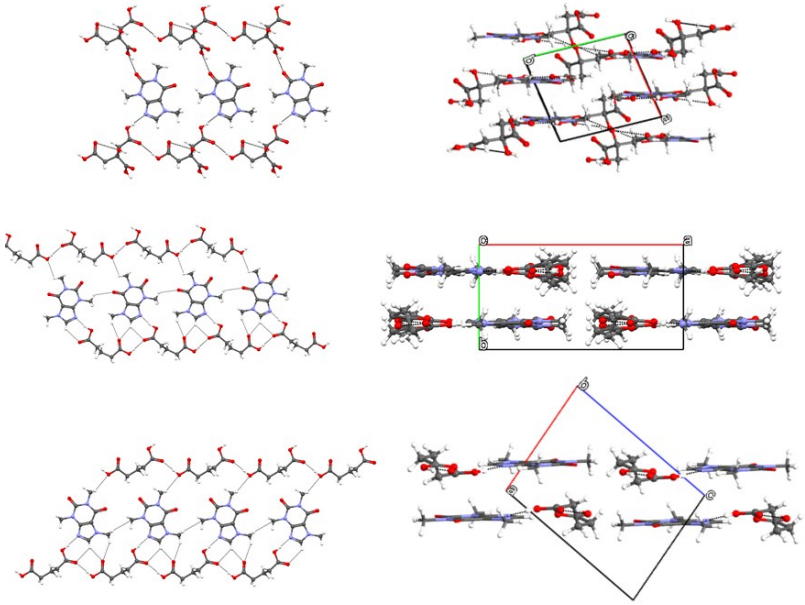


Figure S3. Packing diagrams of **CAF-CA Form I** (top), **CAF-GLU Form I** (middle), **CAF-GLU Form II** (bottom).

S4. Full range PXRD diffractograms

(a) CAF-CA

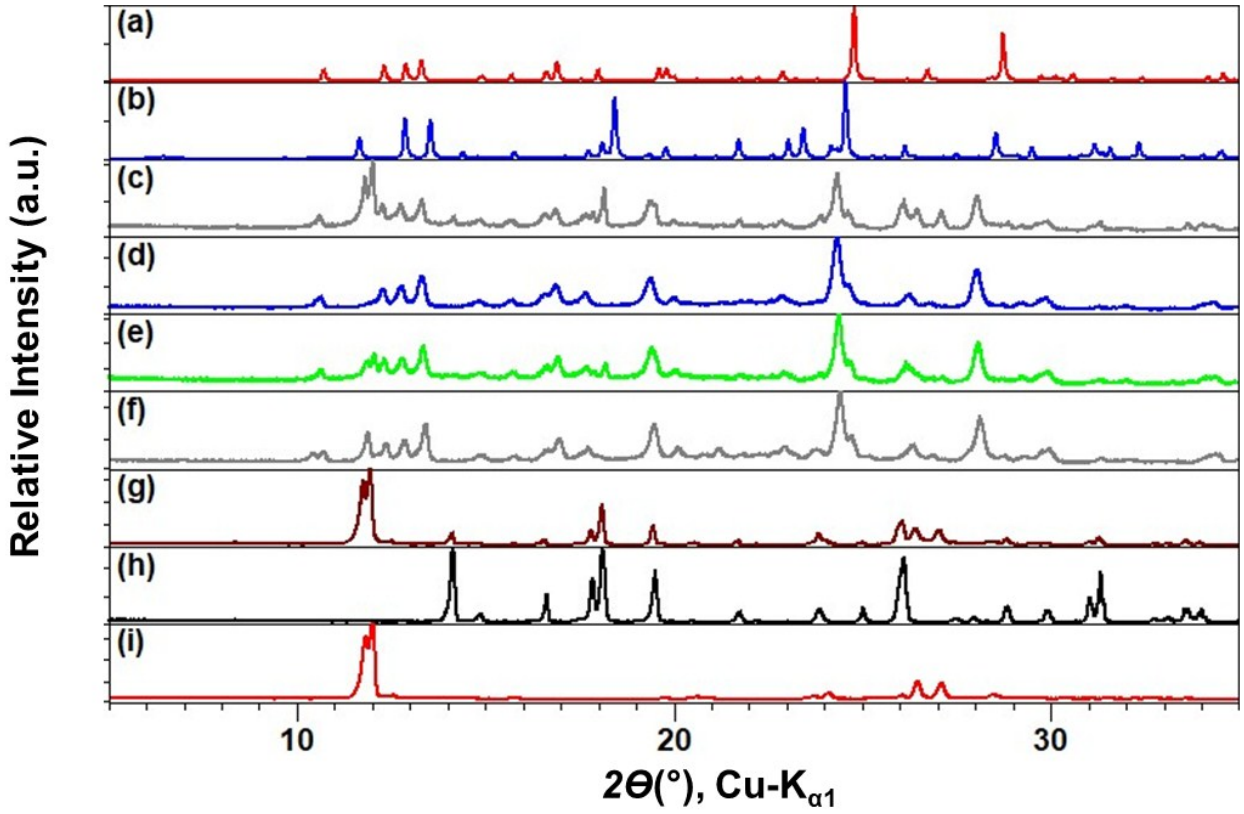


Figure S4a. Simulated pattern of the cocrystal, **CAF-CA**, **Form I** (*P*-1) (a) and **CAF-CA**, **Form II** ($P2_1/c$) (b); the ground powder as obtained from [C_2mim][NTf_2] (c), [C_2mim][BF_4] (d), [OHC_2mim][NTf_2] (e), [OHC_2mim][BF_4] (f); experimental pattern of the powder mixture of **CAF** and **CA** obtained from neat grinding (g), and **CA** (h) and **CAF** (i) used in the grinding experiments.

(b) CAF-GLU: With [C_2mim][NTf_2] homologues

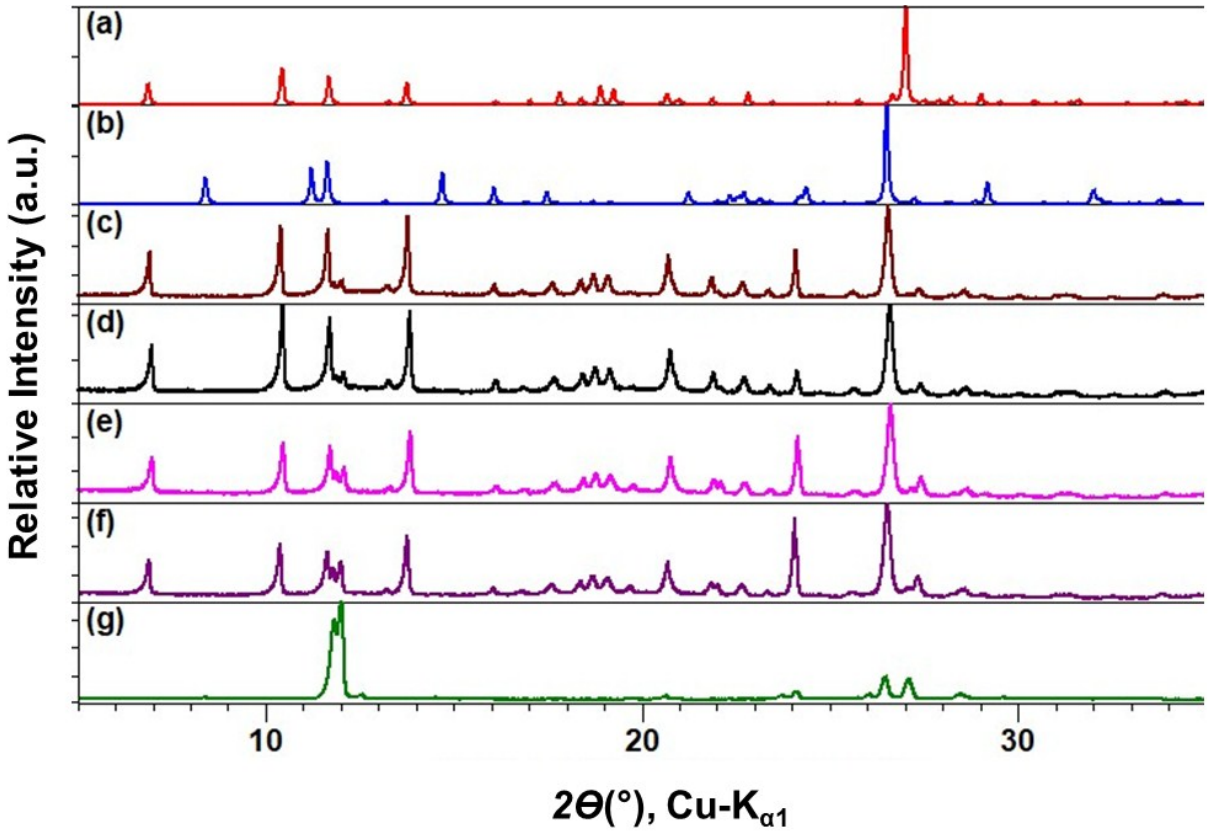


Figure S4b. Simulated pattern of **CAF-GLU Form I** (monoclinic) (a), simulated pattern of **CAF-GLU Form II** (triclinic) (b), the ground powder of **CAF-GLU** as obtained from [C_2mim][[NTf_2] (c), [C_4mim] [NTf_2] (d), [C_8mim] [NTf_2] (e), [C_{12}mim] [NTf_2] (f) and **CAF** (g) used in the grinding experiments.

(c) CAF-GLU: With variation of cations and anions

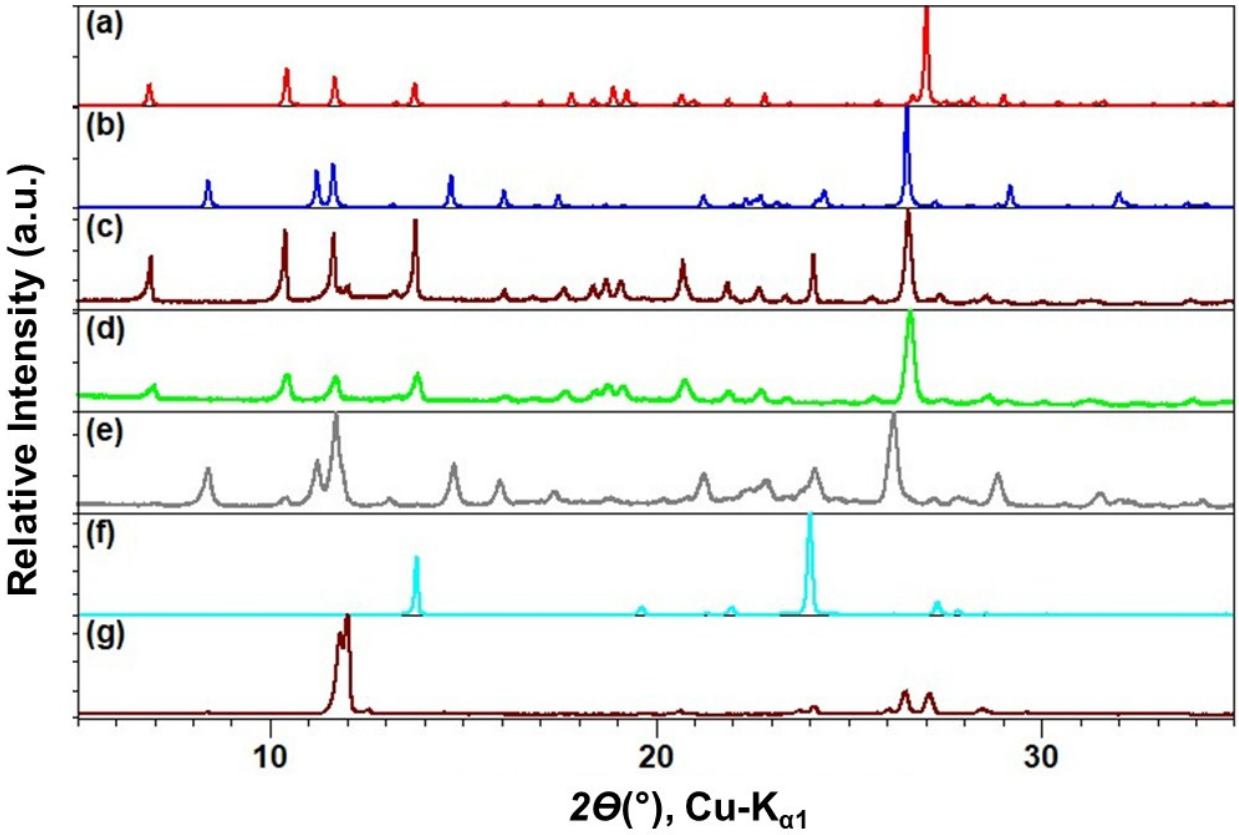


Figure S4c. Simulated pattern of **CAF-GLU Form I** (monoclinic) (a), simulated pattern of **CAF-GLU Form II** (triclinic) (b), the ground powder of **CAF-GLU** as obtained from $[C_2mim][NTf_2]$ (c), $[C_2mim][BF_4]$ (d), [OH C_2mim$][NTf_2]$ (e), [OH C_2mim$][BF_4]$ (f), experimental powder pattern of **GLU** (g) and **CAF** (h) used in the grinding experiments

S5.Water content determination in the ionic liquids used in this study

Ionic Liquid Name	Measurement 1 (ppm)	Measurement 2 (ppm)	Water Content (ppm)	Water Content (%)
$[C_2mim][NTf_2]$	228	230	229±1	0.02
$[C_4mim][NTf_2]$	142	145	143.5±2	0.01
$[C_8mim][NTf_2]$	380	394	387±10	0.04
$[C_{12}mim][NTf_2]$	249	237	243±8	0.02
$[OHC_2mim][NTf_2]$	301	313	307±8	0.03
$[C_2mim][BF_4]$	1018	1048	1033±21	0.10
$[OHC_2mim][BF_4]$	1411	1427	1419±11	0.14